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Measuring contact angles of small spherical particles at planar fluid interfaces by Light Extinction

Imre T. Horváth,[1,a)] Pierre Colinet,[2] and Maria Rosaria Vetrano[1]
[1]*Von Karman Institute for Fluid Dynamics, Chaussée de Waterloo 72, 1640 Rhode-Saint-Genèse, Belgium*
[2]*Université Libre de Bruxelles, Transfers, Interfaces and Processes (TIPs), CP165/67, Avenue Franklin Roosevelt 50, 1050 Bruxelles, Belgium*

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An experimental technique is introduced for measuring the contact angle of small colloidal particles at planar fluid interfaces. The presented light scattering-based method relies on performing two spectral transmittance measurements: one on a particle monolayer standing at the fluid interface and the other on a dispersion of the same particles in a homogeneous medium. The observed shift between the two transmitted spectra is explained in terms of the phase shift parameter, which is then used to determine the particle position relative to the interface and hence the contact angle. The applicability of the technique is demonstrated through simulations and experiments. *Published by AIP Publishing.*
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Particles larger than a few nanometers permanently attach to interfaces between two immiscible fluids, in an attempt to minimize their surface free energy. Such particles are extensively studied due to their technological impact: they are used to stabilize foams and emulsions for the preparation of cosmetics, food products, and pharmaceuticals; they also play a central role in the processes of froth flotation, secondary oil recovery, and waste-water treatment. The key parameter determining the behaviour of colloidal particles at fluid interfaces is the hydrophobicity, quantified by the three-phase contact angle θ (where we assume $0^\circ < \theta < 180^\circ$). The latter is defined as the angle between the tangents to the particle surface and to the fluid interface at the three-phase contact point. When one of the participating fluids is water, it is common to distinguish between hydrophilic ($\theta < 90^\circ$) and hydrophobic ($\theta > 90^\circ$) particles. Several techniques for the contact angle measurement of colloidal particles exist such as the Atomic Force Microscopy (AFM) with a colloidal probe, the Film Trapping Technique (FTT),[1] the Gel Trapping Technique (GTT),[2] the Freeze-Fracture Shadow-Casting Cryo-Scanning Electron Microscopy (FreSCa cryo-SEM),[3] the Film-Calliper Method (FCM),[4] Bessel Beam Microscopy (BBM),[5] and the Multi-angle Single-wavelength Ellipsometry.[6] However, these techniques generally require a specific treatment of the colloidal particles and/or a complex experimental set-up.

In this context, the present communication aims to show that the contact angle of spherical particles at planar fluid interfaces can be determined by means of the analysis of their light extinction spectrum. The introduced method applies to particles from few microns down to a few tens of nanometers. The use of a relatively simple and robust optical setup and the short acquisition time required allows the real-time monitoring of particle contact angles.

The physics of light extinction by small particles is discussed by numerous textbooks,[7] and its application to particle characterization is a subject of recent research.[8,9] When an object, having a different refractive index from its surrounding medium, is present in a light beam path, two main effects occur: the object scatters light in every direction and absorbs some part of the incident energy. Consequently, the energy of the beam propagating in the original direction is decreased, leading to the extinction of light. The most common analytic treatment of light scattering by particles embedded in a homogeneous medium is the Lorenz-Mie theory (LMT), which assumes a spherical shape of the scattering object. The scattering phenomenon is most conveniently treated by quantifying the flow of energy in terms of cross-sections of scattering C_{sca}, absorption C_{abs}, and extinction C_{ext}.[7] The conservation of energy requires that $C_{ext} = C_{sca} + C_{abs}$. It is common to normalize these cross-sections by the geometrical cross-section of the particle to obtain the efficiency factors Q_{sca}, Q_{abs}, and Q_{ext}.

Assuming single scattering, the extinction of an ensemble of particles (particle cloud) can be treated by defining the optical density τ as

$$\tau = \sum_j N_j C_{ext,j}, \tag{1}$$

where N_j is the number of particles of type j per unit volume and $C_{ext,j}$ is the corresponding extinction cross-section. A commonly measured quantity is the transmittance T, which can be computed using the Lambert-Beer law as $T = e^{-\tau L}$, with L being the path length traveled by the light beam within the particle cloud.

The extinction efficiency Q_{ext} of a spherical particle embedded in a homogeneous medium depends on the ratio m between the particle n_p and the medium n_{hm} complex refractive index, i.e., $m = n_p/n_{hm}$. Since the refractive index is a function of the wavelength, Q_{ext} depends on the illumination wavelength λ too, or equivalently on the size parameter $x = D\pi/\lambda$, where D is the particle diameter.

When Q_{ext} is plotted as a function of the size parameter x, it exhibits two distinct characteristics: interference pattern and ripple structure. The ripple pattern is rarely observed experimentally, since it vanishes when particle size polydispersity is present. The interference pattern consists of consecutive

a)Electronic mail: imre.horvath@vki.ac.be

extinction maxima and minima, which are explained by the Optical Theorem[10] as being the consequence of constructive and destructive interferences between the incident and the forward scattered wave. Computing the phase difference α between the incident and the forward scattered waves is equivalent to calculating the phase difference between two light rays: one traveling a particle diameter distance D along the centerline of the particle and the other traveling the same distance in the surrounding medium

$$\alpha^{(\lambda)} = \left[\frac{D \times n_p^{(\lambda)}}{\lambda} - \frac{D \times n_{hm}^{(\lambda)}}{\lambda}\right] 2\pi = \frac{2D\pi}{\lambda / n_{hm}^{(\lambda)}}\left(m^{(\lambda)} - 1\right), \quad (2)$$

where the superscript (λ) signifies that the given quantity is taken at wavelength λ. Eq. (2) requires only the real parts of n_p, n_{hm}, and m; therefore, α is real. The quantity α can be used to universally describe the locations of the maxima and minima of the Q_{ext} function, independently of particle size and relative refractive index, as shown in Fig. 1. α is commonly referred as the phase shift parameter and, as we will see further, it plays a central role in measuring particle contact angles using the Light Extinction technique.

Numerous methods exist for computing light scattering and extinction by particles near- or on (in point contact with) interfaces;[11–13] nevertheless, none of them allows the intersection between the particle and the interface. The rigorous way to compute the influence of the fluid interface on light extinction is to numerically solve the Maxwell equations, e.g., by means of a Finite Element Method (FEM) which generally requires a large computational time. In this work, we propose to use a simple model, which is based on the prediction of the extinction maxima and minima locations of a particle-interface system, by exploiting the concept of phase shift parameter.

A spherical particle trapped at a fluid interface is schematized in Fig. 2. For particles smaller than $\sim 10\mu$m,[14] the body forces (gravity) are negligible compared to the surface tension forces (i.e., a very small Eötvös number); therefore, the deformation of the interface around the particle can be assumed negligible. A single value of immersion depth δ_D

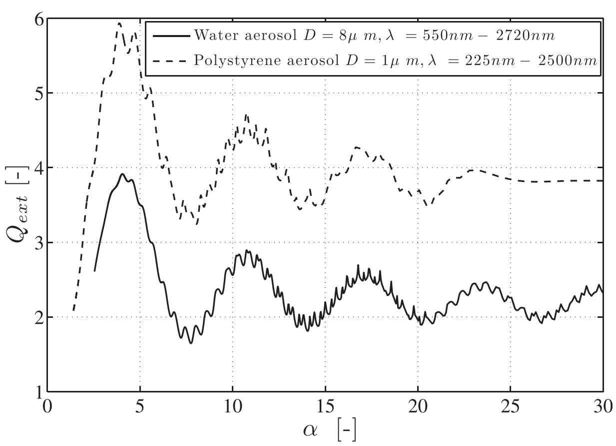

FIG. 1. Extinction efficiencies—computed by the LMT—as a function of phase shift parameter α (Eq. 2) for two different particle sizes and relative refractive indices (i.e., materials). For clarity, an offset equal to 1.5 has been added to the curve of polystyrene.

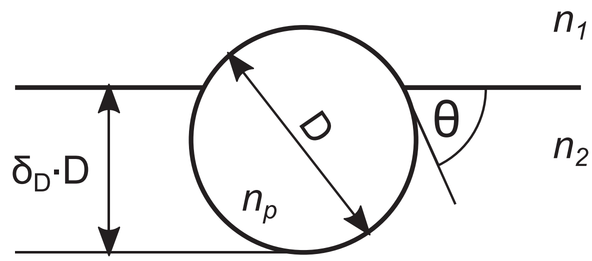

FIG. 2. Geometry of the light scattering system: a spherical particle trapped at a fluid interface. n_1, n_2, and n_p are the refractive indices of *medium 1*, *medium 2*, and the particle, respectively, δ_D is the (dimensionless) immersion depth, and θ is the contact angle.

can be defined as the fraction of D, which is submerged into *medium 2*, as shown in Fig. 2. The phase shift parameter of the particle-interface system α_{if} can be defined as the phase shift between a wave propagating through the plane interface and the other traveling along the centerline of the particle. The phase shifts occurring in *medium 2* and *medium 1* are taken into account separately to yield

$$\alpha_{if} = 2\frac{D\pi}{\lambda / n_1^{(\lambda)}} \times (1 - \delta_D) \times \left(m_1^{(\lambda)} - 1\right) + 2\frac{D\pi}{\lambda / n_2^{(\lambda)}} \times \delta_D \times \left(m_2^{(\lambda)} - 1\right). \quad (3)$$

The symbols $m_2 = n_p/n_2$ and $m_1 = n_p/n_1$ are the relative refractive index of the particle in *medium 1* and *medium 2*, respectively.

It has been shown in Fig. 1 that the maxima and minima of extinction occur at the same phase shift parameter values regardless of the surrounding medium of the particle. By analogy, we here presuppose that the phase shift values of the first extinction maximum for a particle dispersed in a homogeneous medium α_1 and for the same particle at the interface of two media $\alpha_{if,1}$ must be identical, i.e., $\alpha_1 = \alpha_{if,1}$. Due to the difference of refractive index in the surrounding media, the same value of the phase shift should correspond to different wavelengths, leading to a rescaling of the extinction spectrum $C_{ext}(\lambda)$. Our assumption has been numerically verified by comparing FEM computations for a single spherical polystyrene particle at an air-water interface to LMT computations of the same particle in a uniform medium.

The considered polystyrene particle has a diameter D = 1053 nm. Using the LMT and assuming the particle to be embedded in a water bulk, it is possible to obtain the $C_{ext}(\lambda)$ spectrum represented by a dashed line in Fig. 3. The refractive indices of polystyrene and water are extracted, respectively, from Refs. 15 and 16. The same particle is then assumed to be trapped at the air-water interface, and the FEM method is used to obtain the $C_{ext}(\lambda)$ spectra also plotted in Fig. 3 at penetration depths δ_D equal to 0.25 (square markers), 0.5 (circle markers), and 0.75 (x markers). The spectrum of the same particle embedded in air completes the picture (dashed-dotted line). All the presented spectra show similar characteristics, which rescale as a function of the immersion depth, confirming the prediction of the presented simplified model. One may compare, e.g., the spectrum of a particle embedded in water and the one corresponding

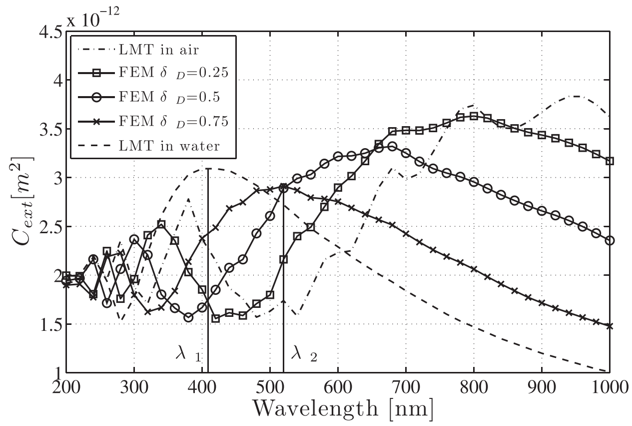

FIG. 3. Extinction spectra obtained using LMT and FEM for a single Polystyrene spherical particle.

to $\delta_D = 0.75$ to find that the maxima are shifted by about $\Delta\lambda = 111\,\text{nm}$ ($\lambda_1 = 409\,\text{nm}$ and $\lambda_2 = 520\,\text{nm}$).

The evaluation of the particle contact angle θ can be done by taking advantage of the extinction spectrum shift due to the influence of the fluid interface. Indeed, θ can be computed directly from δ_D, using geometrical relations, from which the particle diameter D cancels out, showing that the knowledge of particle size is not needed for the contact angle measurements

$$\theta = \cos^{-1}(2\delta_D - 1). \tag{4}$$

To determine the immersion depth δ_D two spectral transmittance measurements are needed: one with the particles dispersed in a homogeneous medium (with refractive index n_{hm}) and the other with the particles forming a monolayer on the interface between *media 1* and *2*. The light beam used for the Light Extinction measurement has to pass through the monolayer perpendicular to its plane. See the supplementary material[17] for further explanation on the extinction spectroscopy experiments.

Solving equation $\alpha = \alpha_{if}$ finally yields δ_D

$$\delta_D = \frac{\frac{\lambda_2}{\lambda_1}\left(n_p^{(\lambda_1)} - n_{hm}^{(\lambda_1)}\right) - \left(n_p^{(\lambda_2)} - n_1^{(\lambda_2)}\right)}{n_1^{(\lambda_2)} - n_2^{(\lambda_2)}}, \tag{5}$$

where λ_1 and λ_2 are the wavelengths of the chosen characteristics when dispersed in homogeneous medium and when trapped at the interface, respectively.

A first verification of the quality of our approach is proposed here using simulated spectra shown in Fig. 3. Introducing the values of $\lambda_1 = 409\,\text{nm}$, $\lambda_2 = 520\,\text{nm}$, and the media refractive indices into Eq. (5), a penetration depth value of $\delta_D = 0.766$ is obtained, which is rather close to the initial value of $\delta_D = 0.75$ used in the FEM calculations. The contact angle obtained by means of Eq. (4) is then $\theta = 57.9°$, which is also close to the one imposed for the FEM simulation (60°). The discrepancy in the penetration depth and hence the contact angle value is a consequence of the limited wavelength resolution of the FEM calculation which needs a long computation time.

The proposed model is also verified experimentally. Spherical polystyrene particles (Polysciences, Inc.) with a

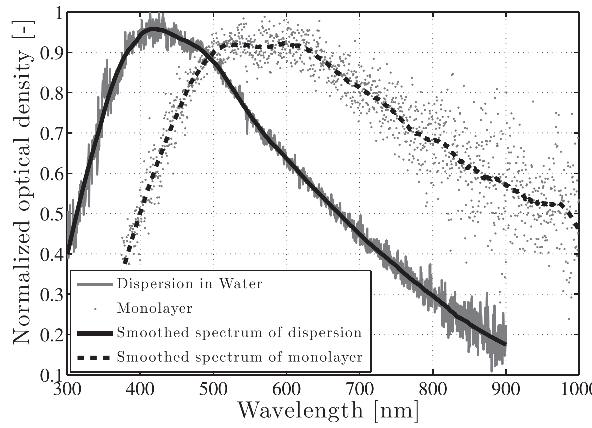

FIG. 4. Experimental normalized (raw and smoothed) optical density spectra of the aqueous Polystyrene (1053 nm) suspension (continuous line) and of the monolayer at the air-water interface (dots).

monodisperse size distribution (mean diameter $D_m = 1053\,\text{nm}$ and standard deviation $\sigma = 0.01\,\mu\text{m}$) are mixed to pure water. The suspension optical density τ—which is related to the extinction spectrum by means of Eq. (1)—is deduced from the measured transmittance spectrum and is reported in Fig. 4. The optical density of a monolayer of the same particles, prepared using a spreading technique,[14] is also measured and reported in Fig. 4. Here again, a shift of the spectrum is observed; the maximum value of each curve can be estimated in $\lambda_{ex_1} = 430\,\text{nm}$ and $\lambda_{ex_2} = 580\,\text{nm}$, leading to a value of $\delta_D = 0.696$ for the immersion depth and a corresponding contact angle of $\theta = 66.9°$. The latter value can be considered realistic for hydrophilic polystyrene particles at an air-water interface, since similar values can be found in the corresponding literature[18] (63°). The experimental spectra as functions of the phase shift parameter corresponding to both systems (Eqs. (2) and (3)) are presented in Fig. 5 and overlap, as expected.

The present communication demonstrates the possibility of measuring *in-situ* the contact angle of spherical particles at the planar fluid interfaces using their light extinction spectrum. It is demonstrated that (a) the light extinction spectra of particles at interfaces depend on the particle immersion depth and that (b) the phase shift parameter can be used to

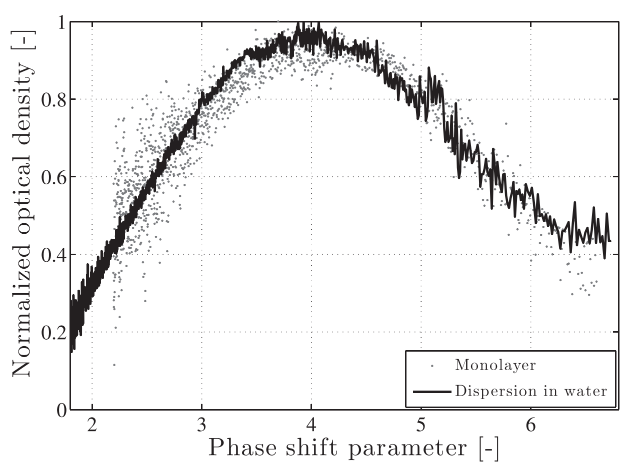

FIG. 5. Experimental normalized optical density spectra of the aqueous polystyrene suspension (continuous line) and of the monolayer at the air-water interface (dots), plotted as a function of phase shift parameters.

retrieve the particle immersion depth hence the contact angle of spherical particles. The main potential of the presented method is its application for studying the dynamics of particle wettability. The method may be extended to study non-spherical particles, as well as single particles; however, assessing the limits and the accuracy of the method will be the central element of future work.

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